

Document made available under the Patent Cooperation Treaty (PCT)

International application number: PCT/GB05/000802

International filing date: 04 March 2005 (04.03.2005)

Document type: Certified copy of priority document

Document details: Country/Office: GB
Number: 0404903.7
Filing date: 04 March 2004 (04.03.2004)

Date of receipt at the International Bureau: 02 May 2005 (02.05.2005)

Remark: Priority document submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b)



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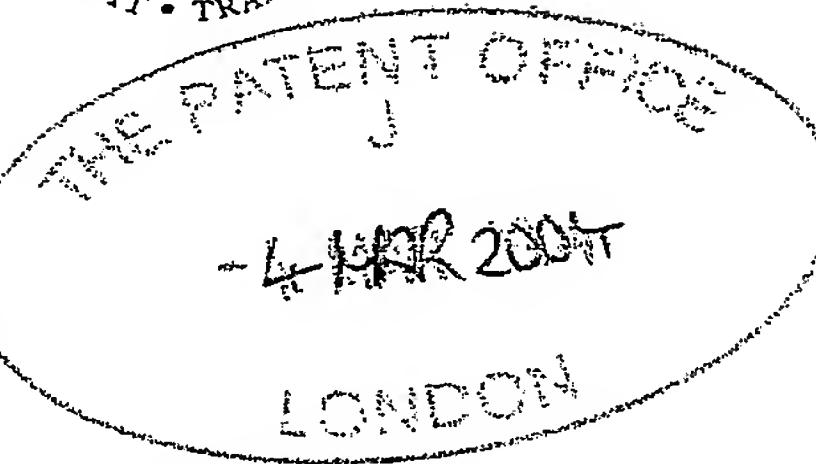
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4. Title of the invention

CARBON NANOTUBE AGGLOMERATES

5. Name of your agent *(if you have one)*

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CARBON NANOTUBE AGGLOMERATESField of the Invention

The invention relates to combinations of carbon nanotubes and redox active materials,
5 particularly for use in electrodes and electrochemical sensors. More particularly, the invention
relates to agglomerates comprising carbon nanotubes and also to their possible uses in the
manufacture of electrodes and electrochemical sensors, particularly pH meters.

Background of the Invention

10 The solid state electrochemistry of a pure organic solid abrasively immobilised onto the surface
of an electrode and which is in contact with an electrolyte solution must take place at the three
phase boundary between the electrode surface|organic solid|solution interface. Concomitant ion
insertion from the solution phase into the crystal to maintain charge neutrality upon
oxidation/reduction must occur. Figure 1 schematically depicts, with the white shading, this
15 three-phase boundary at which transfer of electrons can occur.

However, since electron transfer can only occur at this three-phase boundary, the electroactive
surface area of each individual crystal is restricted to a very small area which is in contact with
both the electrode surface and the solution.

Accordingly, another approach has been adopted, as discussed in Ian Streeter et al, *Journal of*
20 *Solid State Electrochemistry*, submitted for publication (not yet accepted) 2004. This involves
abrasively immobilising a physical mixture of the organic solid and graphite powder onto the
surface of a bppg electrode, as shown in Figure 2.

The electroactive surface area of the electrode shown in Figure 2 is greater than that shown in
Figure 1. This is because not only can an electrode surface|organic solid|solution three phase
25 boundary be formed, but where the carbon particles are in contact with the organic solid crystals
an additional carbon particle | organic solid | solution three phase boundary is formed, thus
allowing increased charge transfer. However, while electroactivity is improved using this
method, the degree of contact between the graphite particles and the organic crystals is restricted
by the size of the graphite particles.

It is an object of the present invention to improve the electrodes discussed above. In particular, having regard to the limitations of the prior art, it is an object of the invention to provide electrodes having improved electroactivity.

5 Summary of the Invention

According to a first embodiment of the invention there are provided agglomerates for use in electrochemical sensors. The agglomerates comprise carbon nanotubes dispersed in a binder, wherein the binder is a redox active material. The carbon nanotubes are preferably multi-walled carbon nanotubes (MWCNTs).

10 According to a second embodiment of the invention, there are provided electrodes for use in electrochemical sensors. The electrodes comprise carbon nanotubes and a redox active material disposed on a substrate. The carbon nanotubes and redox active material in this embodiment need not be mixed in the form of an agglomerate. Instead they may simply be abrasively immobilised on the surface of the substrate. However, it is preferred that the carbon nanotubes and redox active material are disposed on the electrode in the form of an agglomerate, as described above in the first embodiment of the invention. Furthermore, it is again preferred that the carbon nanotubes are in the form of MWCNTs.

15 The electroactivity of these electrodes is greater than prior art electrodes. As a result, a smaller amount of material is required to achieve the same response and hence the electrodes themselves can be reduced in size, allowing for miniaturisation of the electrochemical sensors in which they 20 are employed.

25 The invention also provides an electrochemical sensor comprising a working electrode and a counter electrode, wherein the working electrode comprises carbon nanotubes and a redox active material disposed on a substrate. It is preferred that the sensor also comprises a reference electrode. Again, it is preferred that the carbon nanotubes and redox active material are disposed on the electrode in the form of the agglomerate described above.

Also described is a method for preparing an agglomerate for use in electrochemical sensors. This method comprises dispersing multi-walled carbon nanotubes in a binder, wherein the binder is a redox active material. This agglomerate can then be used in a method for preparing an electrode,

which method comprises providing a substrate and applying carbon nanotubes and a redox active material to the surface of the substrate.

The agglomerates and electrodes described above can be used in electrochemical sensors. Such sensors can be used to monitor a number of different species, such as pH, carbon monoxide, 5 hydrogen sulphide, oxygen, carbon dioxide, metal ions etc. The sensors are particularly useful in the measurement of pH, a measurement that is important in a number of fields, such as environmental, chemical, waste water, industrial and effluent.

Brief Description of the Figures

10 Figure 1 is a schematic diagram showing the regions where the formation of a three-phase boundary may occur when a redox active material such as an organic crystal is immobilised on the surface of an electrode.

15 Figure 2 is a schematic diagram showing the regions where the formation of a three-phase boundary may occur when a redox active material such as an organic crystal is mixed with carbon particles and immobilised on the surface of an electrode.

Figure 3 is a schematic diagram showing the regions where the formation of a three-phase boundary may occur when a redox active material such as an organic crystal is mixed with carbon nanotubes and immobilised on the surface of an electrode. For clarity, the electrode surface is not shown.

20 Figure 4 is a schematic diagram showing the regions where the formation of a three-phase boundary may occur when a redox active material such as an organic crystal is agglomerated with carbon nanotubes and immobilised on the surface of an electrode. For clarity, the electrode surface is not shown.

25 Figure 5 is an SEM image of abrasively immobilised nanotubes dispersed on the surface of a bppg electrode.

Figure 6 is an SEM image of abrasively immobilised agglomerates of multi-walled carbon nanotube and 9,10-phenanthraquinone (MWCNT-PAQ agglomerates) on the surface of a bppg electrode.

Figure 7 is a magnified SEM image of an MWCNT-PAQ agglomerate.

Figure 8 is a digital image of a bppg electrode after abrasive immobilisation of pure PAQ crystals.

Figure 9 is a digital image of a bppg electrode after abrasive immobilisation of a physical
5 mixture of PAQ crystals and multi-walled carbon nanotubes (MWCNTs).

Figure 10 is a digital image of a bppg electrode after abrasive immobilisation of an MWCNT-PAQ agglomerate.

Figure 11 is the overlaid cyclic voltammograms recorded from each material pictured in Figures
8, 9 and 10, allowing a comparison of the magnitude of peak currents compared to the amount of
10 material visibly present on the surface of the bppg electrode.

Figure 12 is the cyclic voltammograms showing 20 repeat cycles (scan rate 50 mV s^{-1}) in pH 6.8 buffer of a) MWCNT-PAQ agglomerates on bppg, and b) agglomerates of multi-walled carbon nanotubes and 1,2-naphthaquinone (MWCNT-NQ agglomerates) on bppg. A cyclic voltammogram recorded after replacing the buffer with fresh solution is overlaid in each case.

15 Figure 13 is the cyclic voltammograms at varying scan rates ($25\text{-}900 \text{ mV s}^{-1}$) recorded in pH 6.8 buffer of a) MWCNT-PAQ agglomerates on bppg, and b) MWCNT-NQ agglomerates on bppg. The inserts show plots of peak current against scan rate.

Figure 14 is overlaid oxidative and reductive square wave voltammograms recorded in a range of buffers (pH 1.0, pH 4.6, pH 6.8, pH 9.2, pH 12.0) at 20°C of a) MWCNT-PAQ agglomerates on
20 bppg, and b) MWCNT-NQ agglomerates on bppg.

Figure 15 is overlaid square wave voltammograms of a) MWCNT-PAQ agglomerates on bppg, and b) MWCNT-NQ agglomerates on bppg in pH 6.8 buffer at varying temperatures (20, 30, 40, 50, 60 and 70°C)

25 Figure 16 is overlaid oxidative and reductive square wave voltammograms of MWCNT-NQ agglomerates in a range of buffers (pH 1.0, pH 4.6, pH 6.8, pH 9.2 and pH 12.0) at 70°C .

Detailed Description of the Invention

By preparing electrodes having carbon nanotubes and redox active materials applied to a substrate, electroactivity is significantly improved because greater contact with the surface of the redox active material is achieved. In effect, the nanotubes act as "molecular wires" forming numerous three phase boundaries between the nanotube|redox active material|solution. When an agglomerate of nanotubes and redox active material is prepared even greater electroactivity is achieved. In this case the nanotubes are cemented together in bundles by the redox material so that they not only run along the surface, but also into and through the agglomerate. At every point of contact between the organic solid, nanotube and the solution, a three-phase boundary is formed. This results in a much larger electroactive surface area compared to the prior art.

Thus, an advantage of the present invention is that the electroactive area is increased, meaning that a smaller amount of material is required in order to achieve the same effect. As a result, the electrodes, as well as the sensors in which these electrodes are employed, may be reduced in size. Miniaturisation of sensors increases the number of applications for which they can be applied. For example, they could be used in biomedical applications where it may be necessary to introduce them into the patient's body. Alternatively they could be used for other applications where sensing apparatus must be used in confined spaces. Miniaturisation also allows for greater portability of the sensors.

The relative proportions of the nanotubes and redox active material used in the invention can be varied by the person skilled in the art. When a mechanical mixture of nanotubes and redox active material is immobilised on a substrate the ratio of these components is preferably 10:1 to 1:10 by mass, more preferably 5:1 to 1:5, more preferably 1:2 to 2:1. In the case where the components are present on the substrate in the form of an agglomerate, the relative proportions may vary significantly. In principle there is no lower limit to the amount of carbon nanotubes present.

The individual components and aspects of the invention will now be described in more detail.

Carbon Nanotubes

Carbon nanotubes (CNTs, also referred to herein as nanotubes) have been known for a number of

years, having been discovered in 1991 (see S. Iijima, *Nature*, 1991, 356, 354). One field that has seen a large expansion in the study and use of nanotubes is electrochemistry. Carbon nanotubes are particularly useful in this field due to their noted mechanical strength, structure and good electrical conductivity. These properties have been used in electroanalytical applications ranging 5 from catalytic detection and analysis of biological molecules such as dopamine, cytochrome c and carbohydrates, to the sensing of analytes such as hydrogen peroxide, hydrazine and TNT.

Structurally, nanotubes approximate to "rolled up" sheets of graphite and as such are relatively hydrophobic in nature. There are two main configurations of these "rolled up" sheets: single-walled carbon nanotubes and multi-walled carbon nanotubes (MWCNTs). In the present 10 invention either configuration may be used.

Suitable nanotubes include those purchased from Nanolab Inc. (Brighton, MA, USA). The physical properties of the nanotubes can be optimised by the person skilled in the art, although exemplary nanotubes have a diameter of from 1 to 50nm, preferably from 5 to 30nm, and a length of from 1 to 50nm, preferably from 5 to 30nm. Preferably the carbon nanotubes have a 15 relatively high purity, preferably from 80 to 100%, more preferably from 90 to 100%, most preferably from 95 to 100%.

Redox Active Material

The redox active material may be any organic material capable of undergoing electron loss and 20 gain. Preferably the redox active material is a solid phase material. When immobilised onto a substrate, e.g. glassy carbon or a basal plane pyrolytic graphite (bppg) electrode, they undergo concomitant proton and electron loss/gain on oxidation/reduction.

In order to be used in electrochemical sensors, at least a part of the redox active material will need to be sensitive to the species which is to be detected or measured. It is preferred that the 25 electrodes be useful in the manufacture of pH meters, and accordingly it is preferred that the peak potential of the redox active materials depends on the local proton concentration.

The voltammetry of such compounds sensitive to pH, when immobilised as molecular solids onto the surface of an electrode, has been found to exhibit Nernstian behaviour which can be described according to the following Nernst equation:

$$E_p = E_f^0 - \frac{2.3RTm}{nF} pH$$

where E_p / V is the peak potential, E_f^0 / V is the formal potential of the redox couple, R / J K⁻¹ is the universal gas constant, T / K is the temperature and m and n are the number of protons and electrons involved in the redox process respectively. In the materials tested in the Examples 5 which follow, m and n are often equal to 2.

Accordingly, by studying the voltammetric response of these compounds, for example using cyclic voltammetry or square-wave voltammetry, a linear response of peak potential to pH would be expected.

The redox active material can comprise more than one compound. For example, the material 10 may comprise a chemically sensitive redox material and a chemically insensitive redox material.

In this embodiment, the chemically insensitive redox material serves as a reference material. By measuring the potential difference between the current peaks for the chemically sensitive and chemically insensitive redox materials, the concentration of the species to be measured can be determined.

15 Alternatively, the redox active material may comprise more than one chemically sensitive material which is sensitive to the same species. By measuring the potential difference between the current peaks for the chemically sensitive materials compared to that of the reference electrode, a more accurate concentration of the species to be measured can be obtained.

The redox active materials used in the example are preferably hydrophobic, have a low solubility 20 in water. This allows them, when an agglomerate is being manufactured, to mix with the carbon nanotubes in solution and results in the agglomerate precipitating out of solution when an excess of aqueous solution is added.

Suitable redox active materials include quinones and anthracenes, for example 9,10-anthracene, 25 9-nitroanthracene, phenanthraquinone (PAQ) and 1,2-napthaquinone (NQ). Other materials that can be used include azobenzene, diphenylamine, methylene blue, 3-nitrofluoranthene, 6-nitrochrysene and thionin.

The Agglomerate

The agglomerate of the invention comprises nanotubes and a binder, wherein the binder is a redox active material. The nature of the nanotubes and redox active material may be as described above.

5 The agglomerate is made by dispersing the nanotubes in a binder. The preferred method comprises combining the nanotubes and binder material in a solvent, and then precipitating the agglomerate out of the solution. In particular, the method may comprise:

- 10 (1) combining the carbon nanotubes and the binder in a solvent;
- (2) adding an excess of aqueous solution in order to cause precipitation of the agglomerate out of the solvent; and
- (3) recovering the agglomerate.

Preferably the solvent is a hydrophobic solvent, comprising small organic molecules. The solvent should be chosen such that the redox active compound and the carbon nanotubes are both soluble within it. Suitable solvents include all common organic solvents such as acetone, acetonitrile and 15 dimethyl formamide.

The agglomerate preferably comprises the carbon nanotubes and redox active material only, with no other materials present. However, the agglomerate may contain some impurities such as residual solvent, left as a result of a process by which the agglomerate is produced. Preferably these impurities comprise less than 1 wt% of the agglomerate, more preferably less than 0.5 wt%. 20 The precise level of impurities which is acceptable in the agglomerate will depend upon how the impurities affect the voltammetry of the agglomerate.

The size of the agglomerates depends upon the nature and proportions of the components used in their preparation and the conditions of the process by which they are prepared. However, exemplary agglomerates may be approximately 10 μm in diameter and consist of bundles of nanotubes running into and throughout an amorphous molecular solid which binds the 25 agglomerate together.

The Substrate

The substrate onto which are applied the carbon nanotubes and redox active material may be any

substrate conventionally used in the manufacture of electrodes. For example, the substrate may be a basal plane pyrolytic graphite (bppg) electrode or glassy carbon, metal electrodes such as gold or platinum, or optically transparent electrodes such as those comprising ITO. The substrate preferably has good electrical contact with the carbon nanotubes, and also has a surface such that
5 good coverage with the carbon nanotubes and redox active material can be achieved.

The Sensor

The structure of the sensor will depend upon its final application, and hence depends upon the substance which it is to measure and the environment in which measurement will take place.

10 Known sensor structures may be employed in conjunction with the agglomerates and electrodes described herein.

Exemplary sensors may have a two or three terminal arrangement. Thus, they may comprise a working electrode of the invention and a combined counter and reference electrode, or a working electrode, counter electrode and a reference electrode. The reference electrode and counter
15 electrode can be any conventional electrodes known in the art.

The materials used in the sensor depend upon which species the sensor is intended to measure and the environment in which the sensor is to be used. In order to modify the sensor to be sensitive to a different species it is simply required for the skilled person to substitute the redox active material with a different redox active material sensitive to the species which is to be
20 measured.

Examples

In order to demonstrate that agglomerates according to the invention can act as electrochemical sensors, the voltammetric response of a number of agglomerates has been studied using cyclic voltammetry and square wave voltammetry. The following examples describe the use of such
25 sensors as pH meters.

EXAMPLE 1: Formation of nanotube agglomerates and their abrasive immobilisation onto
the surface of basal plane pyrolytic graphite

Reagents and Equipment

All reagents were obtained from Aldrich (Gillingham, UK) with the exception of potassium chloride which was obtained from Riedel de Haën (Seelze, Germany) and were of the highest grade available and used without further purification. All aqueous solutions were prepared using deionised water from an Elgastat (Elga, UK) UHQ grade water system with a resistivity of not less than 18.2 MΩ cm. All cyclic voltammetric measurements were made after degassing the solution with pure N₂ gas (BOC Gases, Guildford, Surrey, UK) for 30 minutes and unless otherwise stated were recorded at a temperature of 20 ± 2 °C.

Multi-walled carbon nanotubes (MWCNTs) with purity ~95% were purchased from Nanolab Inc. (Brighton, MA, USA) and were used without further purification.

Solutions of known pH in the range pH 1-12 were made up in de-ionised water as follows: pH1, 0.1 M HCl; pH 4.6, 0.1 M acetic acid + 0.1 M sodium acetate; pH 6.8, 0.025 M Na₂HPO₄ + 0.025 M KH₂PO₄; pH 9.2, 0.05 M disodium tetraborate; pH 12 0.01 M sodium hydroxide. These 15 solutions contained in addition 0.1 M KCl as additional supporting electrolyte. pH measurements were performed using a Jenway 3030 pH meter.

Electrochemical measurements were recorded using a μAutolab computer controlled potentiostat (Ecochemie, Netherlands) with a standard three-electrode configuration. All experiments were 20 carried out using a double-walled glass cell of volume 25 cm³ thermostatted to the desired temperature (20-70 °C) through circulation of water from a heated bath. A basal plane pyrolytic graphite electrode (bppg, 0.20 cm², Le Carbone Ltd., Sussex, UK) acted as the working electrode (see below). A platinum coil acted as the counter electrode and a saturated calomel electrode as the reference electrode (SCE, Radiometer, Copenhagen) completed the cell assembly.

25 Unless stated otherwise cyclic voltammograms were recorded using the following parameters: step potential 2 mV, scan rate 50 mV s⁻¹. Square wave voltammetric parameters were as follows: frequency 12.5 Hz, step potential 2 mV and amplitude 25 mV. Scanning electron microscopy (SEM) was conducted using a Jeol 6500F instrument.

It is worth noting that the toxicology of both 9, 10-phenanthraquinone and 1, 2 napthaquinone

has not yet been fully investigated. Both compounds may be harmful, or irritant by skin contact or inhalation and are suspected carcinogens.

5 Formation of nanotube agglomerates and their abrasive immobilisation onto the surface of basal plane pyrolytic graphite

Agglomeration of MWCNTs with either 9, 10-phenanthraquinone (PAQ) or 1, 2-naphthaquinone (NQ) was achieved by mixing 50 mg MWCNTs with 10 cm³ of a 10 mM solution of either PAQ or NQ in acetone and slowly adding 25 cm³ of 0.1 M HCl + 0.1 M KCl aqueous solution. The reaction mixture was stirred continuously for 2 hours in a beaker and then filtered by suction 10 after which it was washed with distilled water to remove the acid and salt. It was then air-dried by placing inside a fume hood for 12 hours and finally stored in an airtight container until required.

15 The agglomerates of nanotubes and either PAQ or NQ were then abrasively immobilised onto the surface of the bppg electrode prior to characterisation. This was done by initially polishing the electrode on glass polishing paper (H00/240), after which it was polished on silicon carbide paper (P1000C) for smoothness. The nanotube-PAQ or nanotube-NQ agglomerates were then mechanically immobilised onto the bppg electrode by gently rubbing the electrode surface on a fine filter paper (Whatman) containing the agglomerates.

20 **EXAMPLE 2: Characterisation of the nanotube agglomerates**

First the formation of the agglomerates was verified using SEM and CV and then the immobilisation of the agglomerates onto the surface of the bppg was confirmed voltammetrically using CV.

Determination of the degree of agglomeration

25 In order to verify that agglomerates of PAQ or NQ with MWCNTs are formed rather than a physical mixture of microcrystals of either PAQ or NQ and MWCNTs, scanning electron microscopy (SEM) was employed. Each material was imaged separately after abrasive immobilisation onto the surface of a clean bppg electrode had been carried out. First the SEM

image of pure MWCNTs (with no organic solid present) was recorded (Figure 5). Next the SEM images of the MWCNTs, which had been modified according to the procedure given in section 2.2 were recorded for comparison (Figure 6 and 7).

These images confirm that unlike unmodified MWCNTs on bppg which are dispersed evenly over the surface (Figure 5), the MWCNT-PAQ material had indeed formed agglomerates of nanotubes cemented together in bundles by the PAQ (Figure 6 and 7) as shown schematically in Figure 4.

Finally, the cyclic voltammograms (overlaid in Figure 11) of PAQ crystals, a mechanical mixture of MWCNTs and PAQ crystals, and the MWCNT-PAQ agglomerates were recorded separately in pH 6.8 buffer after abrasive immobilisation onto the surface of a bppg electrode. In each case a nearly symmetrical wave shape with similar peak heights was observed at ca -0.23 V vs. SCE, with a slight peak to peak separation of ca. 20 mV.

Experimentally it is impossible to control the exact amount of material that is abrasively immobilised onto the surface of the bppg electrode. However, as is apparent from Figures 8, 9 and 10, visibly less of the MWCNT-PAQ agglomerate material was needed on the surface of the electrode to give similar magnitudes of peak currents as either the PAQ crystals on their own. Figure 6 shows that the actual surface coverage of the bppg electrode by the MWCNT agglomerates is sparse. The mechanical mixture of MWCNTs and PAW crystals gives an intermediate result.

A crude calculation of the effective electroactive surface area of the MWCNT-PAQ agglomerate was undertaken. The PAQ molecules were considered to occupy rectangles of area $2.5 \times 10^{-19} \text{ m}^2$ and the number of molecules oxidised or reduced was calculated from the peak area of the corresponding cyclic voltammogram. Thus the approximate electroactive surface area of this material was found to be typically greater than three times that of the bppg electrode itself.

It is worth noting that this crude calculation assumes the area of the electrode surface to be equal to its geometric area. In reality, polished surfaces may have a surface area substantially greater than the geometric area. Furthermore a proportion of the PAQ or NQ binder may not react due to inefficient charge transfer to the electrode surface, as impurities on the MWCNT surface may impair conductivity at the bppg/MWCNT interfacial region. However, even with these limitations in mind the results are still indicative of a significant increase in the electroactive

surface area of the electrode when MWCNT agglomerates are immobilised upon it.

One possible explanation for this is found by considering that one of the advantages of electrodes modified with carbon nanotubes is a larger effective electroactive surface area with obvious analytical benefits. The structure of abrasively immobilised MWCNT agglomerates has been
5 shown (above) to consist of bundles of MWCNTs cemented together in an amorphous organic solid on the surface of a substrate electrode. As discussed earlier, such a structure confers a significantly greater electroactive surface area where three-phase boundaries can be formed than the situation when pure organic crystals or physical mixtures of an organic solid and graphite powder are used. Hence less of the agglomerate material is required to produce signals of similar
10 orders of magnitude as in the other two cases studied above.

Determination of surface immobilisation

The immobilisation onto the bppg surface was confirmed using cyclic voltammetry. The two agglomerates were then studied over the entire pH range pH1-12. The first step in the protocol, once the potential region of the redox process for PAQ or NQ had been determined, was to
15 conduct twenty repetitive scans (the exact potential range of these scans varied between PAQ and NQ and with pH) to ensure the stability of the species. In the case of both MWCNT-PAQ agglomerates and MWCNT-NQ agglomerates a nearly symmetrical wave shape with a slight peak separation that increased with increasing scan rate (see below) was observed at every pH (Figure 12a and 12b). It was found that after twenty repetitive scans the peak currents (which
20 initially were found to decrease slightly) remained stable and that the charges (peak areas) of both the oxidative and reductive peak processes were equal to each other.

The next step in the protocol was to replace the electrolyte solution with fresh solution and record the voltammetric response. The corresponding cyclic voltammogram (overlaid in Figures 12a and 12b) was found to overlay the last scan thereby confirming that the electroactive species
25 remains on the surface of the electrode and is not released to solution. Finally the scan rate was varied from 25 to 900 mV s⁻¹ (Figure 13a and 13b) and a plot of peak current vs. scan rate was found to be almost linear. The peak separation (ca. 20 mV at low scan rate) is close to the ideal zero peak to peak separation for an immobilised, electrochemically reversible species. However,
30 the discrepancy between the experimental and theoretical peak separation, and the deviation from linearity in the plots of peak current vs. scan rate may be tentatively attributed to some slight ohmic distortion and/or electrode kinetic factors. In fact the wave shapes and the variation of

peak potential with increasing scan rate suggest that an electrochemically quasi-reversible system exists over the entire pH range studied.

EXAMPLE 3: Voltammetric response of agglomerates to pH at room temperature

Having established, using cyclic voltammetry in Example 2 above, that a stable, electrochemically almost reversible system is observed for both MWCNT-PAQ and MWCNT-NQ agglomerates over the entire pH range from pH 1 to pH12, square wave voltammetry was utilised as the electrochemical method of probing the system in all the studies detailed below. This has significant advantages as compared to conventional cyclic voltammetry, since it provides a means of carrying out a single sweep which produces a well-defined voltammetric peak due to PAQ and NQ having almost reversible electrode kinetic behaviour. This can therefore aid in the resolution of the MWCNT-PAQ and MWCNT-NQ reduction waves, especially at higher pH where oxygen reduction may compete at a similar potential to that of the redox process of interest. Square wave voltammograms were recorded for MWCNT-PAQ and MWCNT-NQ agglomerates in a range of pH solutions (pH1, 0.1 M HCl; pH 4.6, 0.1 M acetic acid + 0.1 M sodium acetate; pH 6.8, 0.025 M Na_2HPO_4 + 0.025 M KH_2PO_4 ; pH 9.2, 0.05 M disodium tetraborate; pH 12 0.01 M sodium hydroxide) and are overlaid in Figures 14a and 14b respectively. It is apparent from Figure 14a and 14b that as the pH is increased the peak potential of MWCNT-PAQ and MWCNT-NQ shifts to more negative potentials as expected. This behaviour is consistent with that observed for PAQ crystals abrasively immobilised on a bppg electrode.

The corresponding plot of peak potential against pH reveals a linear response from pH 1 to pH12 with a gradient of 55.2 and 53.2 mV/ pH unit for MWCNT-PAQ and MWCNT-NQ respectively, which is reproducible upon repetitive electrode preparations as described earlier. This is close to a Nernstian response as given by the equation discussed earlier and is again consistent with previous studies on carbon powder.

EXAMPLE 4: Voltammetric response of agglomerates to pH at elevated temperature

The effect of temperature on the voltammetric response of the agglomerates was investigated in

order to determine whether the materials might be used as suitable pH probes for high-temperature environments.

One factor to be noted while studying the effect of temperature on the system is how the pH of the solution varies with temperature as the dissociation constants of the components in the buffer 5 solution vary with temperature. To this end three IUPAC buffers (pH 4.6, pH 6.8 and pH 9.2) were utilised that have a known set of pHs at a given temperature. The error due to using pH1 and pH12 solutions of dilute HCl or NaOH respectively for high-temperature studies is negligible as the pH variation with temperature of all buffers is small and these are the extremities of the plot.

10 Square wave voltammograms were recorded for each pH studied in the range pH1 to pH 12 over the temperature range 20-70 °C for both MWCNT-PAQ and MWCNT-NQ. Note that the upper limit of this temperature range was limited by the onset of bubble formation on the electrode as the temperature approached the boiling point of the solution. Figure 15a and 15b show the overlaid square wave voltammograms of MWCNT-PAQ and MWCNT-NQ respectively over the 15 temperature range 20-70 °C in pH 6.8 IUPAC buffer. Similar responses were obtained at every other pH studied. There is a shift of the peak potential to more negative values with increasing temperature which can be attributed in part to a combination of changes in the SCE reference couple, the temperature dependence of the formal potential (E_f^0) and the temperature term in the Nernstian equation discussed earlier. It is worth noting that the peak current initially increases 20 with temperature, but then decreases steadily after 30 °C. In order to investigate the stability of the agglomerates at elevated temperatures cyclic voltammetry was employed at every temperature studied in the range 20-70 °C. Five hundred scans were performed at each temperature on the abrasively immobilised MWCNT agglomerates at a scan rate of 200 mV s⁻¹ and every fifth scan recorded, corresponding to a time interval of ca. 35 seconds. In every case a 25 single, reversible and almost symmetrical wave was observed corresponding to the MWCNT-PAQ or MWCNT-NQ agglomerate as described earlier. From these voltammograms the peak area was measured, which is proportional to the amount of the electroactive species remaining on the surface of the electrode in the form of MWCNT agglomerates. From a plot of peak area against time (not shown) it was apparent that although the signal remains stable for 30 500 scans over ca. 1 hour at 20 °C, at temperatures above 30 °C there is a decrease in the magnitude of the signal. This behaviour is in contrast to chemically adsorbed anthraquinone on graphite

particles, where the magnitude of the signal increases steadily with increasing temperature, but is in agreement with earlier studies of PAQ physically adsorbed onto the surface of graphite particles. This would suggest that the decrease in signal observed at elevated temperatures for MWCNT-PAQ and MWCNT-NQ agglomerates is due to partial dissolution of the agglomerates.

5 However, even at 70°C after 500 scans (ca. 1 hour) an appreciable signal, ca. 10% of the original value, still remains.

Figure 16 shows the overlaid square wave voltammogram for NQ at 70°C showing that an analytically useful response may be obtained at this elevated temperature.

A plot of peak potential vs. pH at each temperature studied yielded a straight line, with R^2 values 10 not less than 0.998, for both MWCNT-PAQ and MWCNT-NQ agglomerates, the gradients of which are given in Table 1. The theoretical gradient as predicted by the Nernst equation is also given in Table 1 for comparison. As can be seen the variation of the gradient of peak potential with pH is not Nernstian and indeed is relatively insensitive of temperature varying by ca 3 mV/pH unit over a temperature range of 50°C. This is advantageous in that it not only 15 demonstrates that these agglomerates may be used as pH sensors at elevated temperatures, but also that they are not greatly affected by quite significant changes in temperature.

Table 1

Experimental gradients of plots of peak potential against pH at each temperature studied for abrasively immobilised MWCNT-PAQ and MWCNT-NQ agglomerates.

Temperature (K)	Theoretical gradient (mV / pH unit)	Experimental Gradient (mV / pH unit)	
		MWCNT-PAQ	MWCNT-NQ
293	58.1	55.2	53.2
303	60.1	55.4	53.4
313	62.1	56.5	53.7
323	64.1	56.7	53.9
333	66.1	56.9	54.9
343	68.1	57.0	56.6

5 As shown in Examples 3 and 4, a linear response of peak potential to pH is observed for both MWCNT-PAQ and MWCNT-NQ agglomerates over the entire pH range and temperature range studied. Furthermore, a comparison of the gradients of a plot of peak potential against pH at each temperature reveals that both MWCNT-PAQ and MWCNT-NQ agglomerates are relatively insensitive to the effects of temperature changes. Such a property is advantageous for pH measurement where samples are obtained at a range of different temperatures.

10

It will be apparent to those skilled in the art that modifications may be made to the invention as described above without departing from the scope of the claims below.

CLAIMS

1. An agglomerate for use in electrochemical sensors, said agglomerate comprising carbon nanotubes dispersed in a binder, wherein the binder is a redox active material.

5

2. An agglomerate according to claim 1 wherein the redox active material has a voltammetric response which is chemically sensitive to the concentration of the species to be detected by the electrochemical sensor.

10 3. An agglomerate according to claim 1 or claim 2 wherein the redox active material is sensitive to the concentration of protons.

15 4. An agglomerate according to any one of claims 1 to 3 wherein the redox active material comprises a further redox active material which is chemically insensitive to the concentration of the species to be detected by the electrochemical sensor.

5. An agglomerate according to any one of claims 2 to 4 wherein the redox active material comprises at least two redox active materials chemically sensitive to the concentration of the species to be detected by the electrochemical sensor.

20

6. An electrode for use in electrochemical sensors, said electrode comprising, disposed on a substrate, carbon nanotubes and a redox active material.

25 7. An electrode according to claim 6 wherein the redox active material is as defined in any one of claims 2 to 5.

8. An electrode according to claim 6 or claim 7 wherein the carbon nanotubes and redox active material are applied to the substrate either in the form of a mechanical mixture, or in the form of an agglomerate as defined in any one of claims 1 to 5.
- 5 9. An electrode according to claim 7 wherein the carbon nanotubes and redox active material are applied to the substrate in the form of an agglomerate.
10. An electrode according to claim 9 wherein the agglomerate is abrasively immobilised on the substrate.
- 10 11. An electrochemical sensor comprising a working electrode and a counter electrode, wherein the working electrode comprises the electrode as defined in any one of claims 6 to 10.
- 15 12. A sensor according to claim 11 further comprising a reference electrode.
13. A sensor according to claim 12, wherein the redox active material is sensitive to the concentration of protons and the sensor is a pH sensor.
- 20 14. A method for preparing an electrode for use in electrochemical sensors, said method comprising providing a substrate and applying carbon nanotubes and a redox active material to the surface of said substrate.
15. A method according to claim 13 wherein the carbon nanotubes and redox active material are applied to the substrate in the form of a mechanical mixture, or in the form of an agglomerate as defined in any one of claims 1 to 5.

16. A method according to claim 15 wherein the carbon nanotubes and redox active material are applied to the substrate in the form of an agglomerate.

5 17. A method according to any one of claims 14 to 16 wherein the step of applying comprises abrasively immobilising the carbon nanotubes and redox material on the substrate.

10 18. A method for preparing an agglomerate for use in electrochemical sensors, said method comprising dispersing carbon nanotubes in a binder, wherein the binder is a redox active material.

15 19. A method according to claim 16 wherein the method comprises the steps of:
1. combining the carbon nanotubes and the binder in a solvent;
2. adding an excess of aqueous solution such that the agglomerate is precipitated out of the solvent; and
3. recovering the agglomerate.

20 20. A method according to claim 18 or claim 19 wherein the redox active material is as defined in any one of claims 2 to 5.

25 21. Use of an agglomerate according to any of claims 1 to 5 or of an electrode according to any of claims 6 to 10 in an electrochemical sensor.

22. Use according to claim 21 wherein the sensor is a pH sensor.

23. Use of an electrochemical sensor according to any of claims 11 to 13 to measure pH.

ABSTRACTCARBON NANOTUBE AGGLOMERATES

An agglomerate for use in electrochemical sensors, said agglomerate comprising carbon nanotubes dispersed in a binder, wherein the binder is a redox active material. Also described is an electrode for use in electrochemical sensors, said electrode comprising carbon nanotubes and a redox active material disposed on a substrate. The carbon nanotubes and redox active material may be disposed on the substrate in the form of the agglomerate described above. The electrodes can be used in electrochemical sensors, and in particular for the measurement of pH.

Figure 1

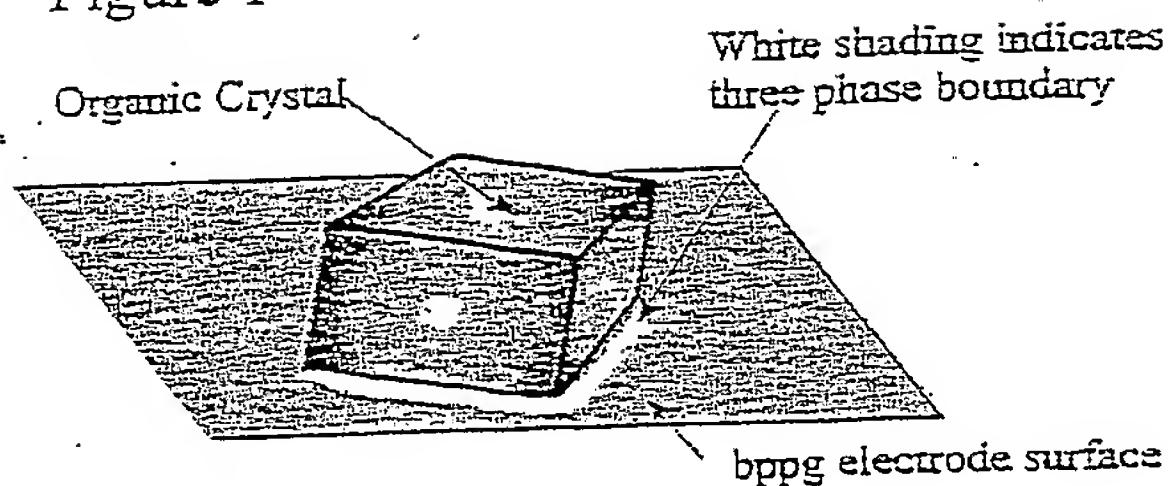


Figure 2

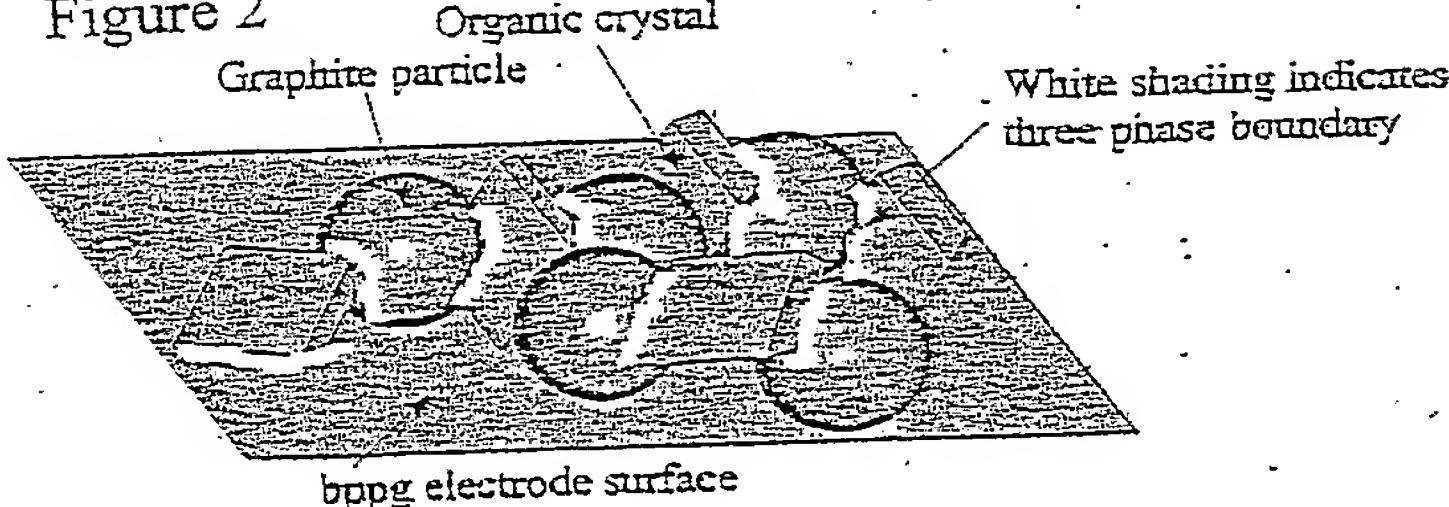


Figure 3

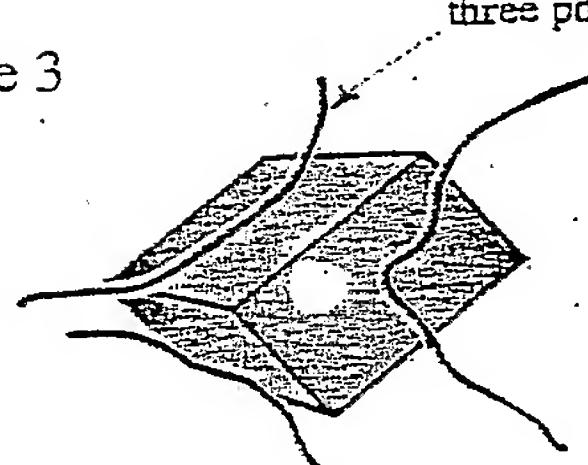
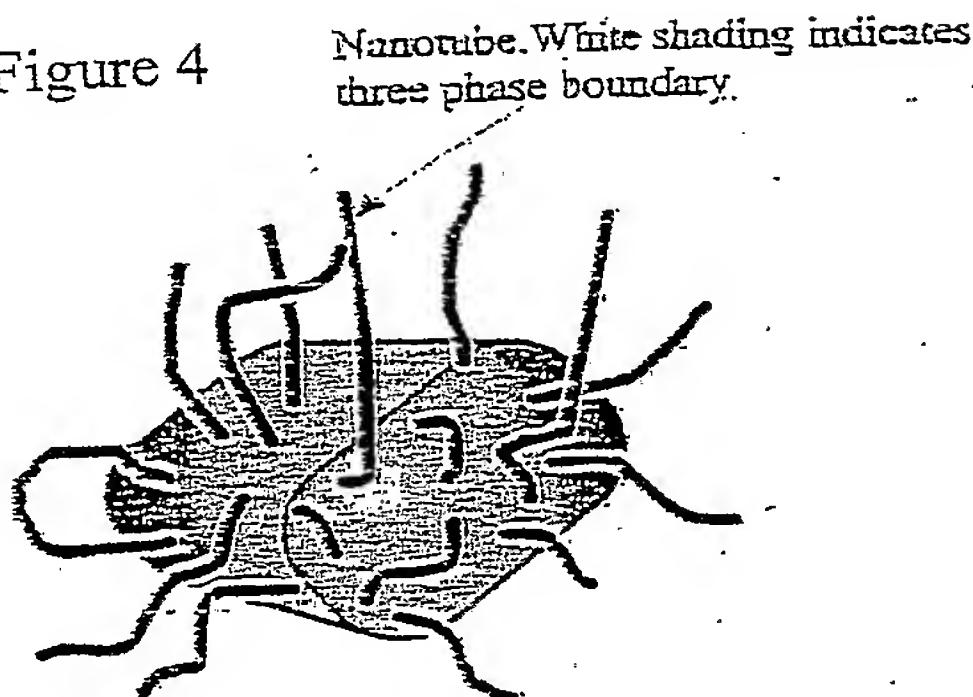


Figure 4



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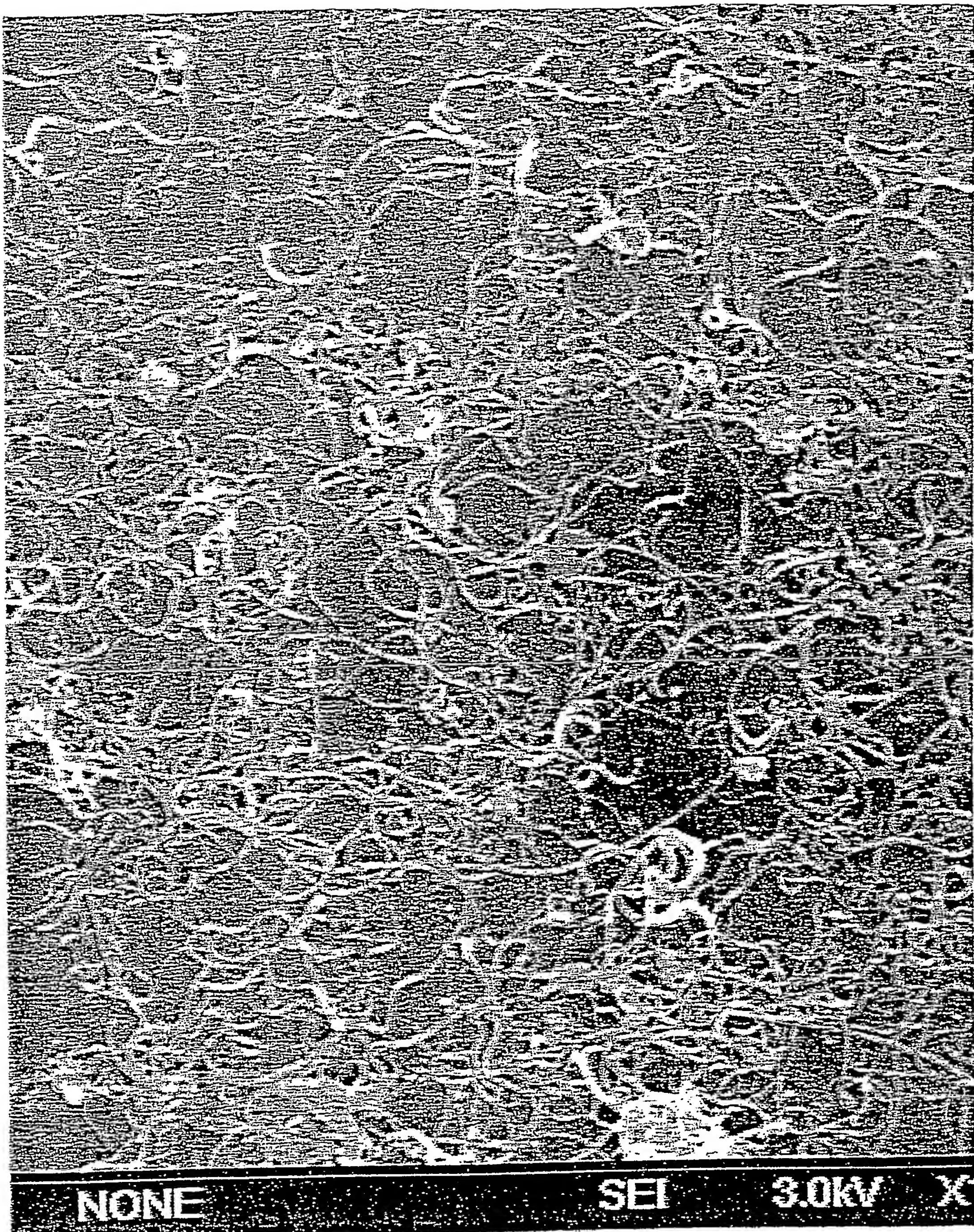


Figure 5

3 / 10

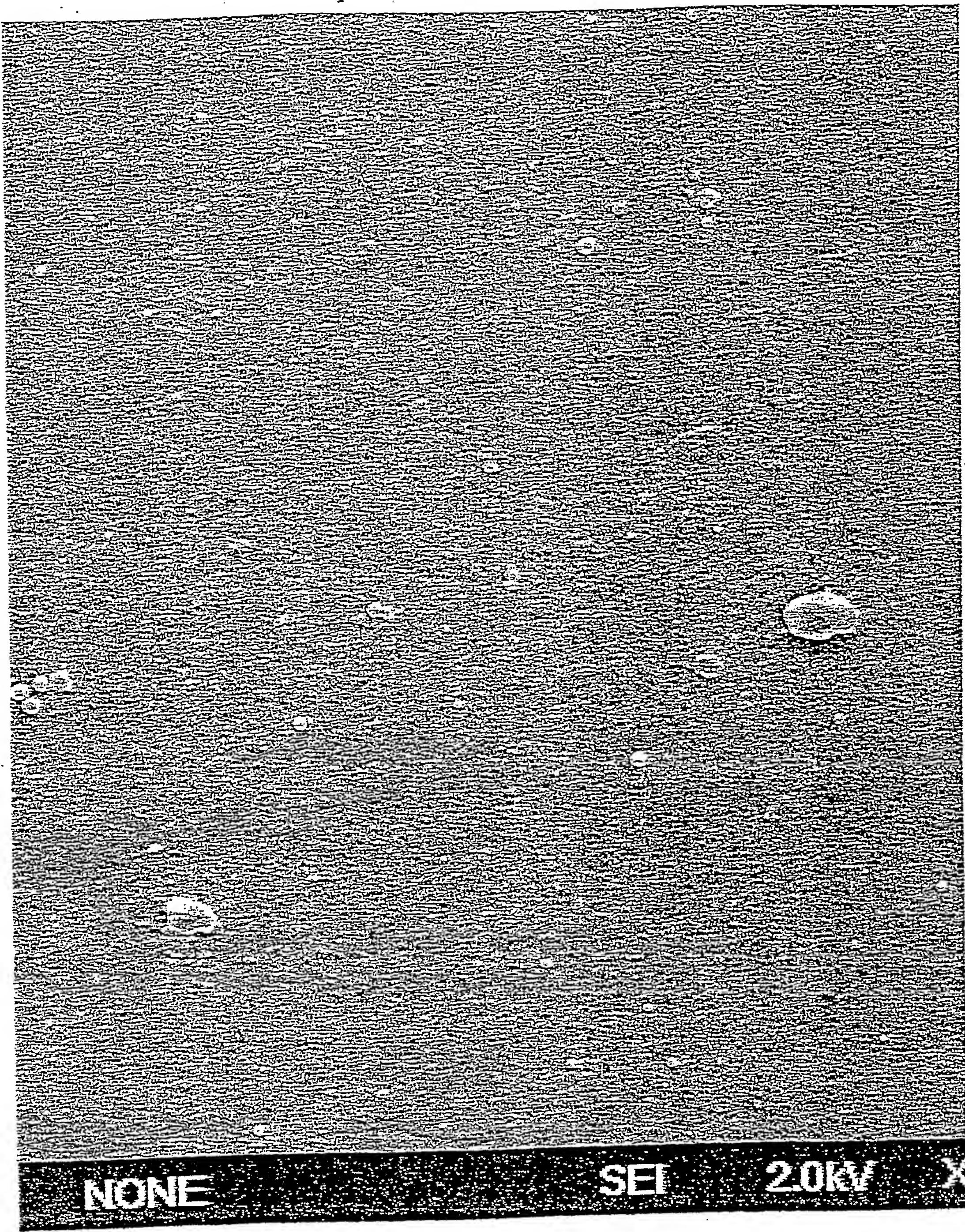
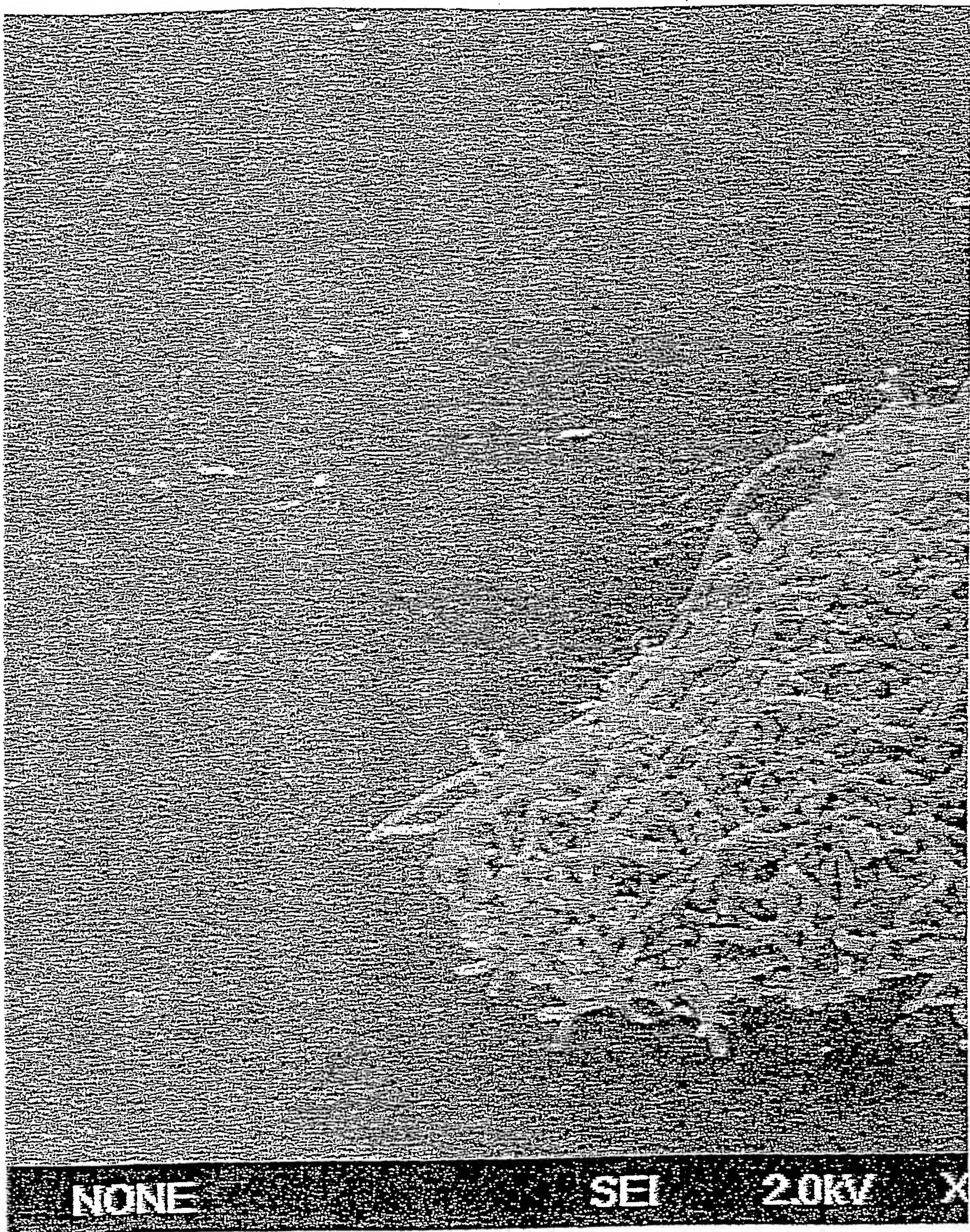


Figure 6

4 / 10



NONE

SEI

20KV

Figure 7

Figure 8

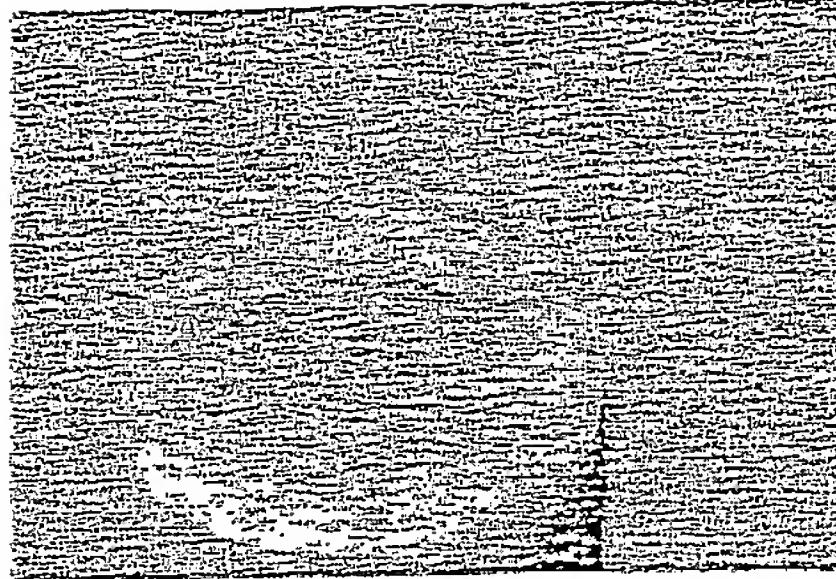


Figure 9

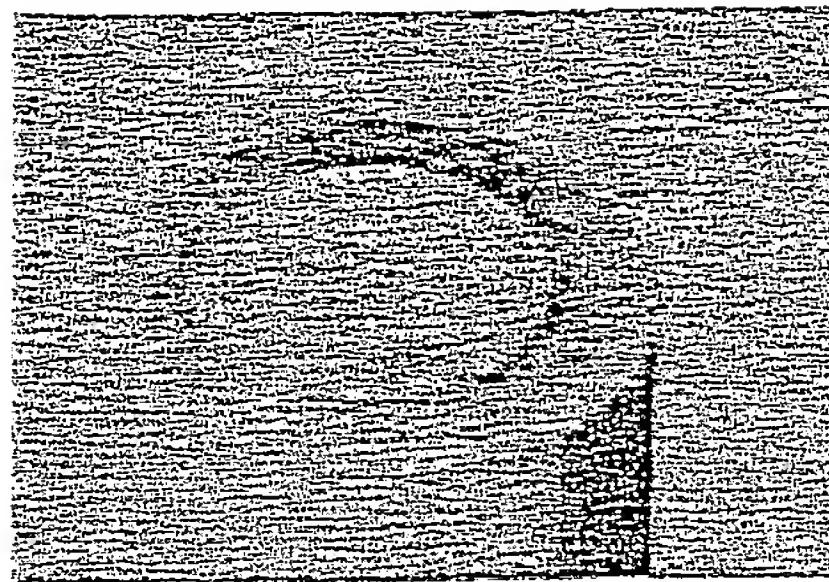


Figure 10

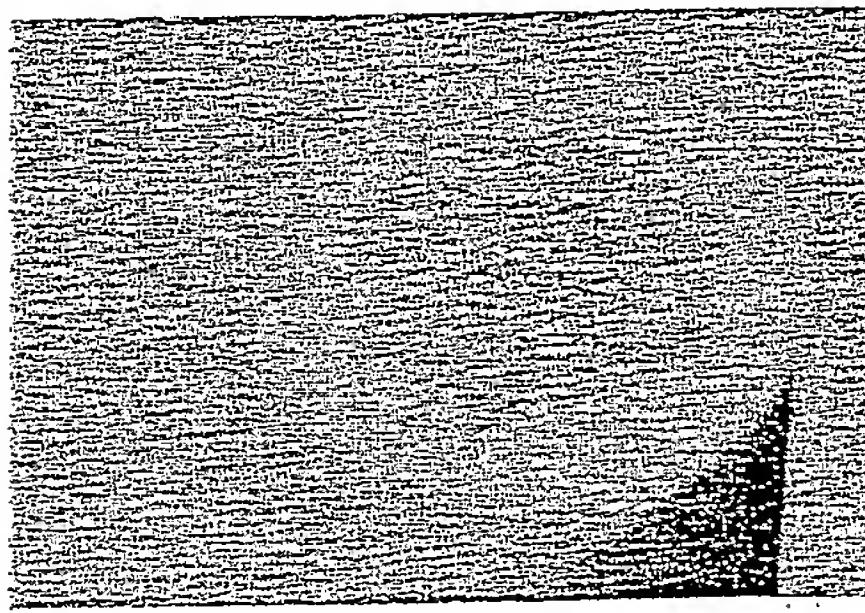


Figure 11

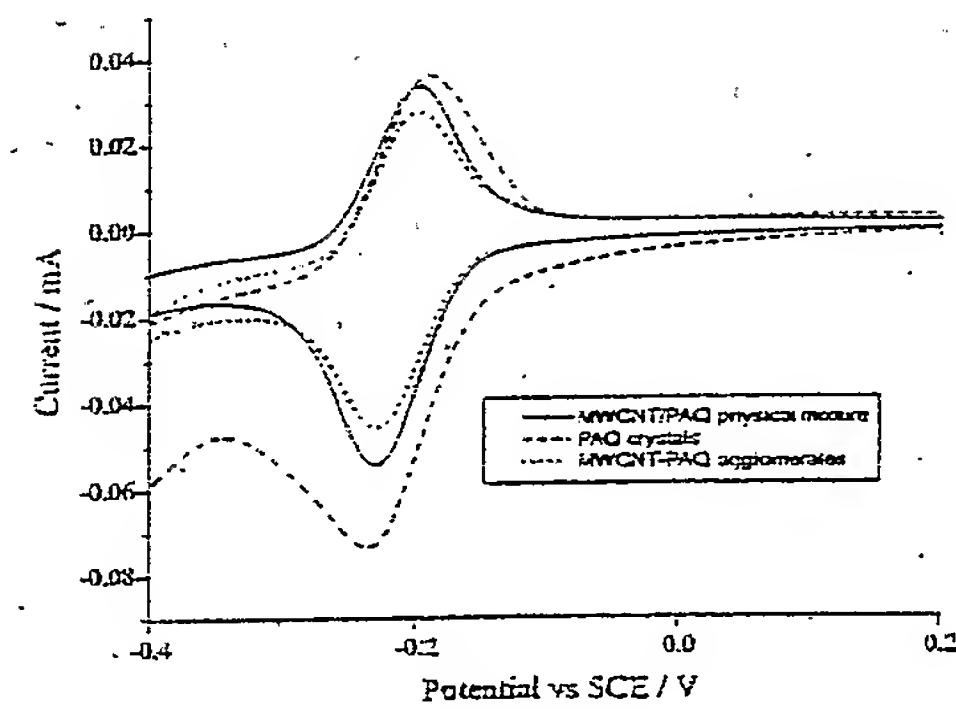


Figure 12

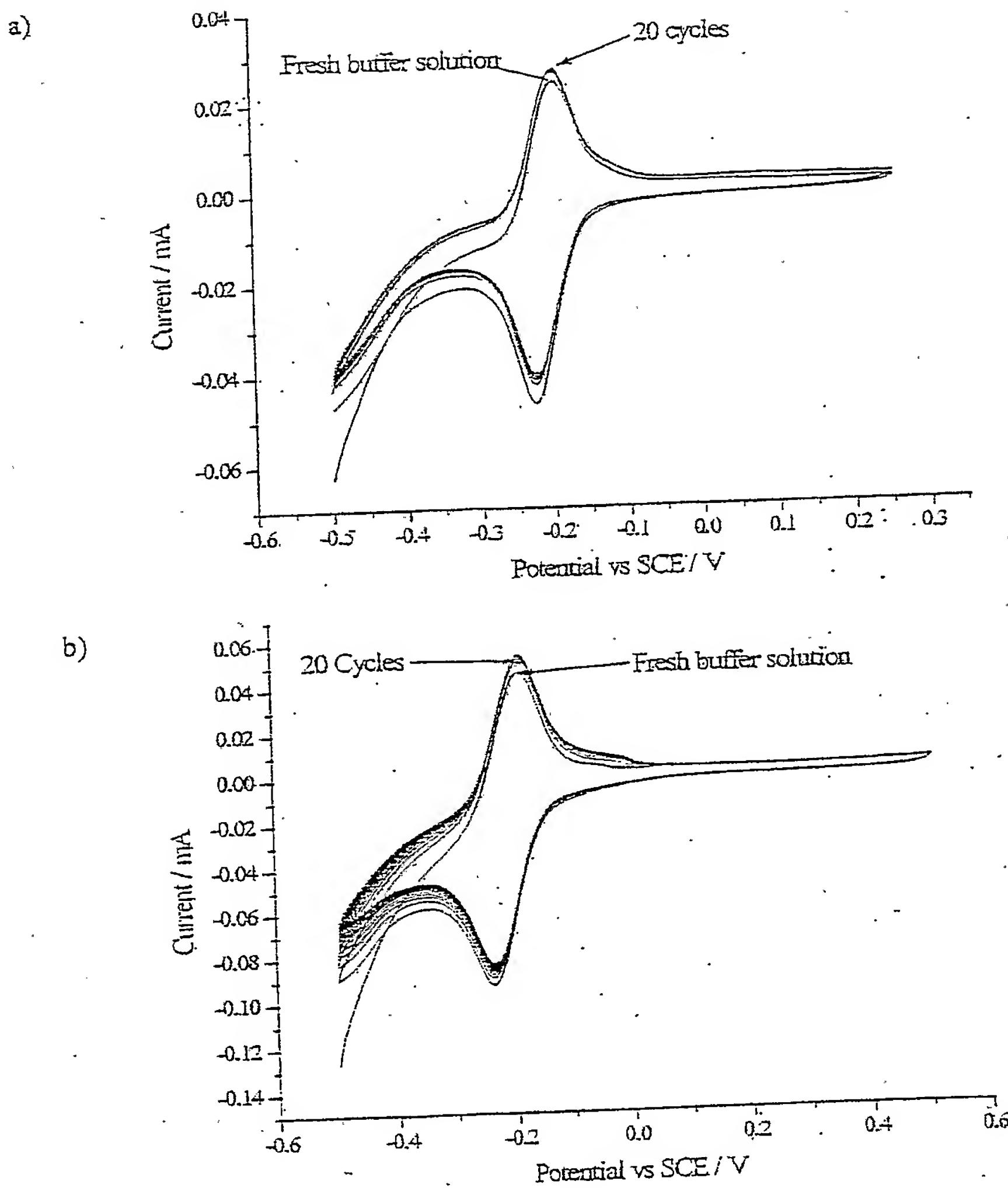


Figure 13

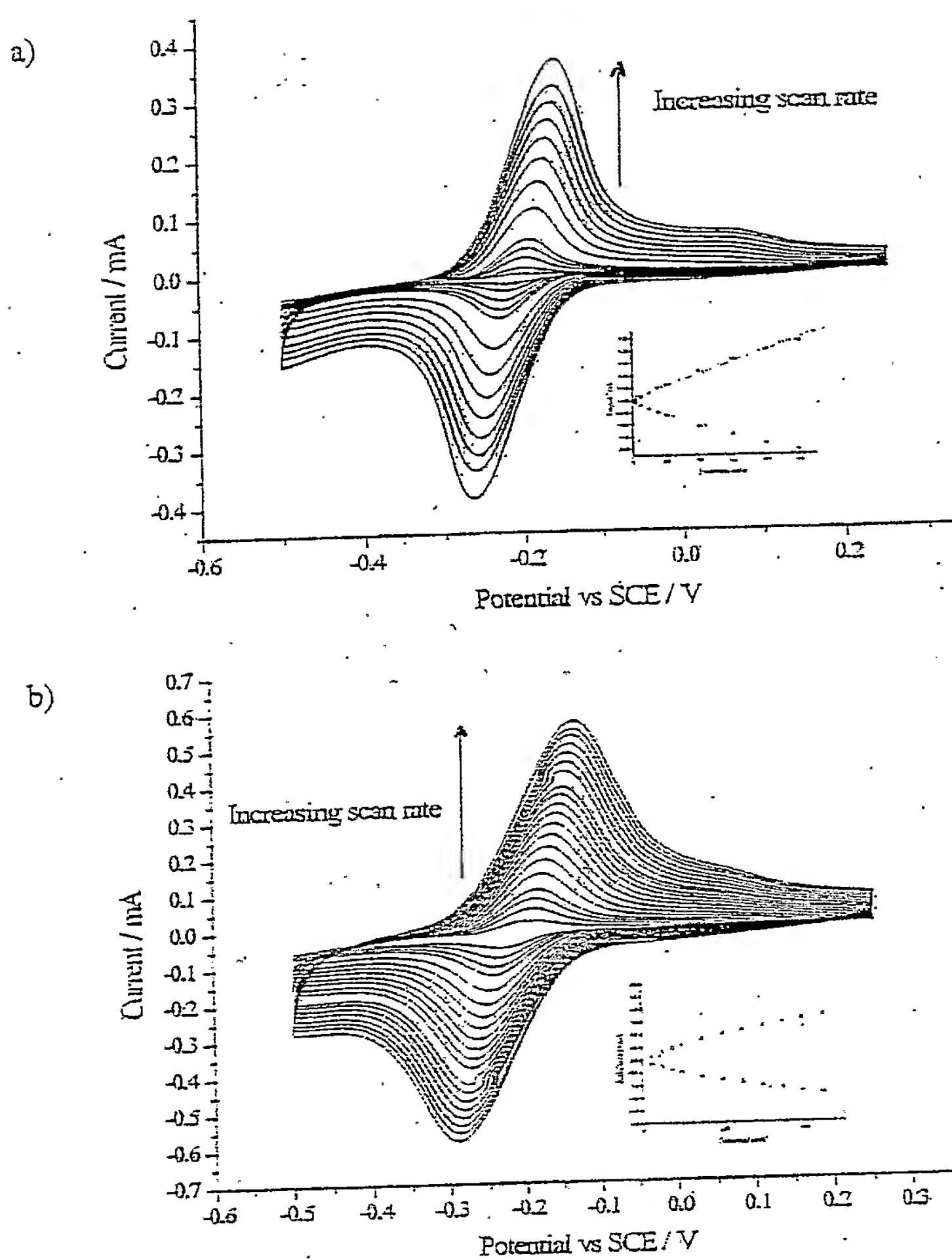


Figure 14

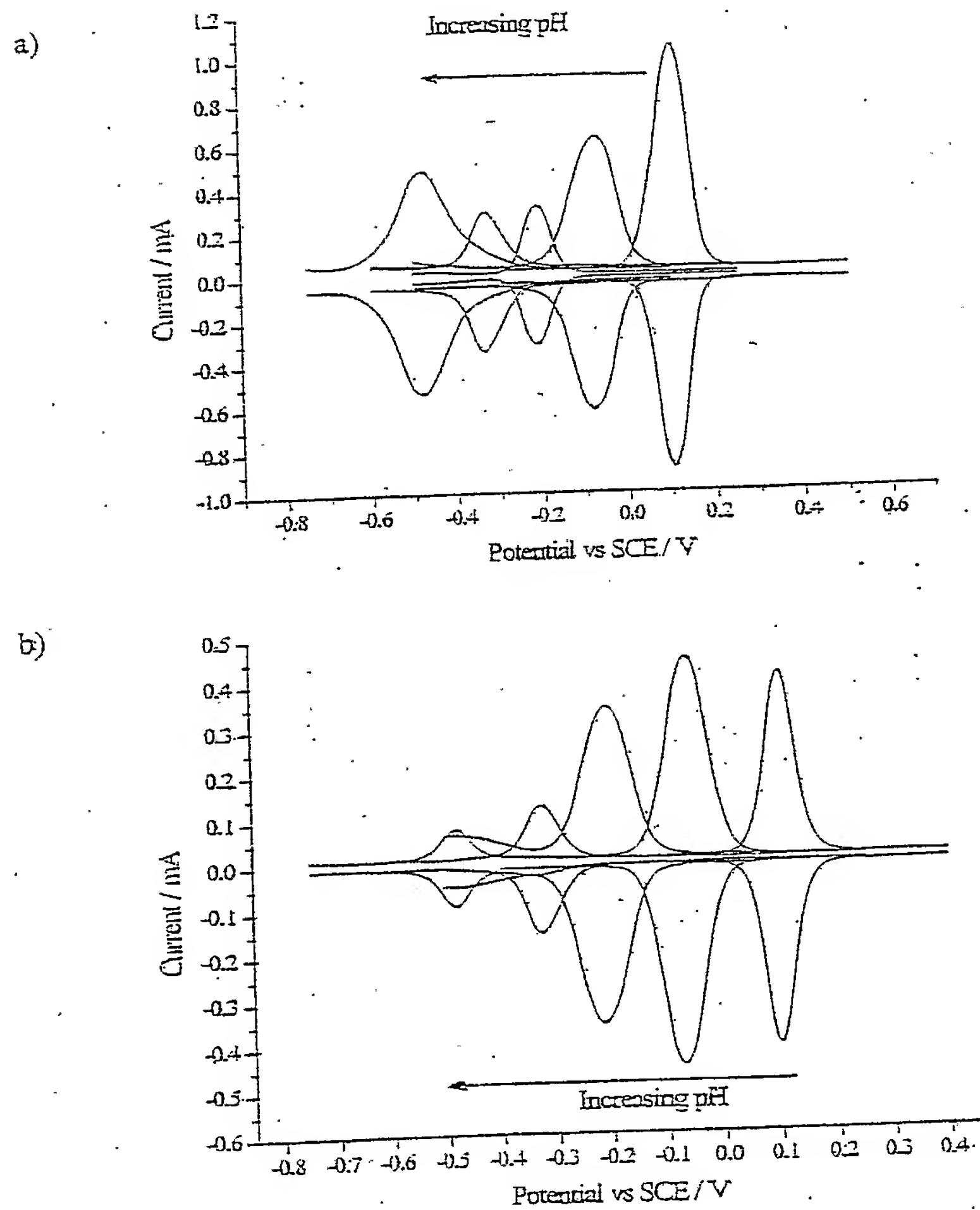
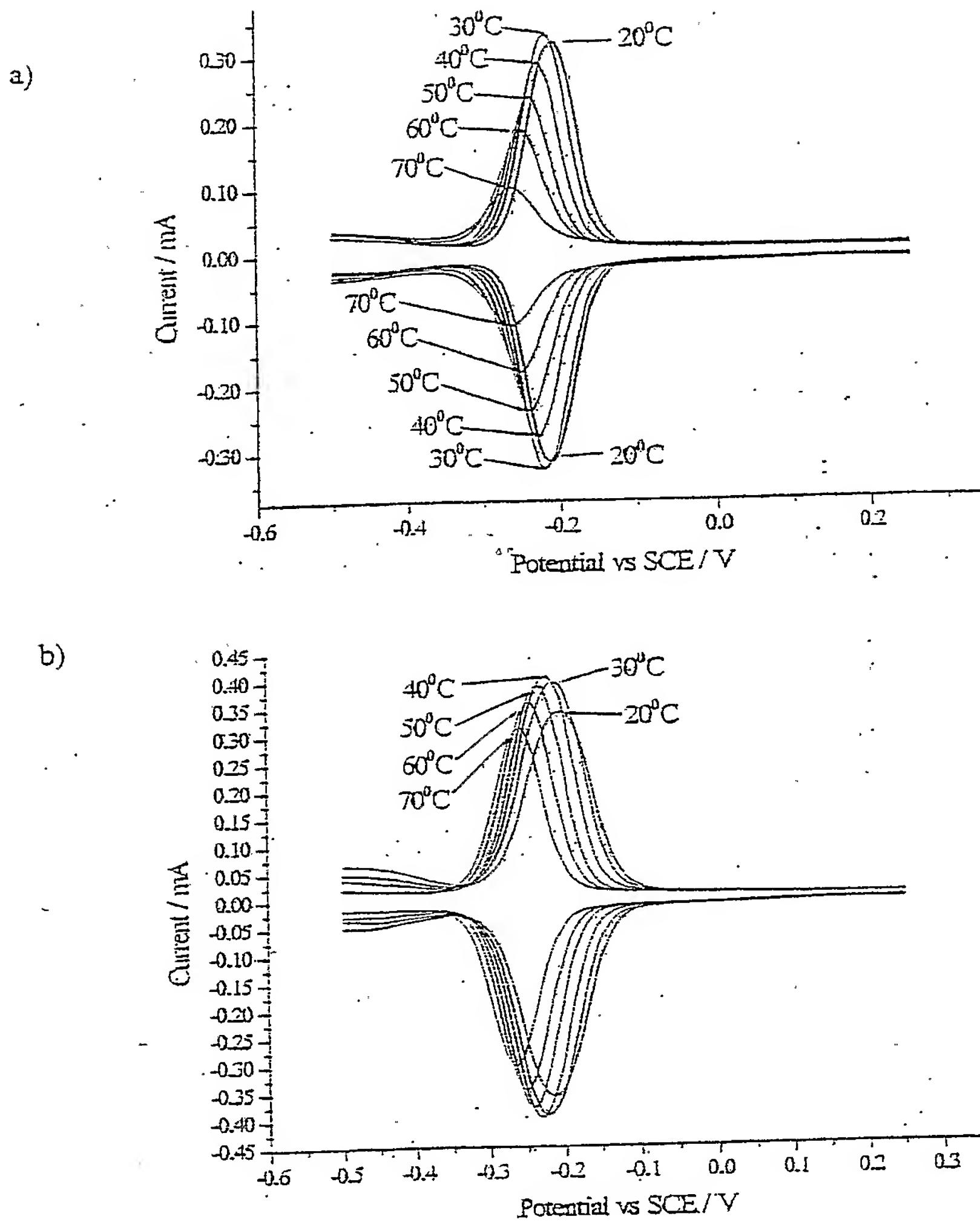


Figure 15



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Figure 16

